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EUROPEAN PATENT APPLICATION

(1) Application number. 83387162.8

(2) Date of filing 21.11.83

(1) Im C1 C 08 F 4/72 C 08 F 4/80, C 08 G 59/68 C 08 G 77/08, C 08 G 2/06 C 08 F 2/50

(S) Priority: 22.11.82 US 443660

(a) Cote of publication of application: 20.05.84 Bulletin 84/22

Designated Contracting States:
CM DE FR GB IT U

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(a) Energy polymerizable composition containing organometallic initiators.

(3) An energy polymerizable composition and process therefore, comprising a cationically polymerizable material and a catalytic thy effective amount of an ionic selt of an organometallic complex cation as polymerization initiator, said ionic selt of an organometallic complex cation being capable of adding an intermediate strength nucleophile or upon photolysis capable of liberating at least one coordination site, said inetal in said organometallic complex cation being selected from elements of Periodic Groups IVB, VB, VIB, and VIIB are disclosed Certain of the organometallic metallic polymerization initiators are novel cationic salts.

Containing Organometallic Initiators Energy Polymerizable Compositions

Technical Field

cationically-sonsitive materials and organometallic complex The present invention relates to a process for employing as polymerization initiator a certain class of the polymerization of cationically-sensitive meterials ionic organometallic compounds. In another aspect, it compounds. In a further aspect, it relates to certain relates to polymerisable compositions containing organometallic polymerisation initiators.

Background Art

the above-mentioned patents teaches the acceleration of the discloses the use of bis- and tris-salicylic soid complexes and carboxylic acids, and U.S. Patent No. 4,237,242 relates The prior art describes various processes for the further known that a metallocene, such as ferrocene, can be of thromium(III) to catalyze the reaction between epoxides acid group-containing polymers with polyspoxides. Each of manganese, iron, etc.) of acetylacetonate type ligands to accelerate the thermally initiated reaction of carboxylic basic amhydrides, organic peroxides, and quinone. It is epoxy materials by use of curing additives such as polydescribed in U.S. Patent No. 3,705,129. U.S. Patent Nos. ambydrides or polymercaptans. U.S. Patent No. 3,867,354 polymerization of apoxy materials. It is known to cure reaction between polyepoxides and polyfunctional curing initiation of c tionic polymeritation, particularly the used as a curing accelerator for epoxy materials and is 3,709,861 and 3,714,006 describe the use of cyclopentadienylasnganese tricarbonyl for the acceleration of the light-catalyzed reaction between polyepoxides and acid additives, but they do not teach the polymerisation of to the use of transition metal complexes (chromium,

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epoxide group-containing compositions not containing a curing additive.

materials, specifically epoxide group-containing meterials, The polymerization of cationically-polymerizable in the absence of curing additives is, bosever, well known Among such processes are those in which the polymerization catalyst (also called sensitiser of initiator) is (1) a radiation-sensitive onlym salt of a Levis acid te-9. dissonium salts as are described in U.S. Patent No.

salts, as are disclosed in U.S. Patent No. 4,055,400); (2) 3,794,576 and U.S. Patent No. 4,000,274; helonium salts as are disclosed in U.S. Patent No. 4,026,705; and the onlum 80c. 100, 996 (1978); and (4) titamocess dichlorids which a disarbonyl chelate compound of a Group Illa-43 element 2-chiorosthylvingl ether as is described by Learijone of salts of Group VIA elements, perticularly the sulfonium salt which is used for the polymerization of tetrahydrofuran as is described by Woodbouse, et al., J. ben. Chem. is disclosed in U.S. Patent No. 4,086,601; (3) a aliver is used for the polymerization of epichlorohydrin and 2

Purposmore, the dicarbonyl chalates are moisture sensitive al., J. Polym, Sci., Chem. Ed. 19, 2033 (1972) and 121d. and dichloribe requires a co-catalyst. aborn-mentioned catalysts are unsatisfactory 'scause without the addition of optical senaitizers they are limited to ultraviolet rediction for polymerisation. 14, 3547 (1976). Compositions containing the

losure of the invention

and the titeno

The present investion provides a process for the utifising as catalyst a cationic compused which is a salt counterion used, the relative thermal stability and wavelength of sensitivity (from 100 to 600 nm) can be adepted of # organometallic complem cation. By selection of the metal and ligands in the erganometallic complex and the polymerization of cationically-sensitive meterials 35

for various applications.

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In accordance with the present invention there re provided onergy-curable compositions comprising:

- al a cationically-polymerizable material and
- Periodic Groups IVB, VB, VIB, VIIB, and VIIIB. a catalytically-effective amount of an ionic phenylphosphine or upon photolysis capable o liberating at least one coordination site, said metal of said organometallic complex sufficient to effect polymerization, said mediate atrength nucleophile such as trisalt of an organometallic complex cation cation being capable of adding an interionic salt of an organometallic complex cation being selected from elements of
- 15. There is also provided a process for the polymerization of cationically sensitive material comprising the steps of:
 - with a catalytically-effective amount of the cation, thereby forming a mixture, and mining the cationically-sensitive material ionic salt of an organometallic complex
- allowing the mixture to polymerise or adding energy to the mixture to effect polymerization thereof.

As used in this applications.

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cationically-polymerizable material at least to a degree to "catalytically effective amount" means a quantity sufficient to effect polymerization of the increase the viscosity of the compusition, and

"intormediate strength nucleophile" means a. chloride, e.g., trialkyl- and triarylphosphines, trialkylnucleaphile intermediate in atrength between hydride and and triarylphosphitos, pyridimes, and anilines.

Detailed Description of the Invention

cations useful in the compositions and processes of the The ionic salts of the organometallic complex invention are compounds having the formula:

7x 0,(97)(57)(97) (pr(pg7)(pg7)(pg7)) wherein Ma, Mb, Mc, and Md represent metal atoms which may ments of Periodic Groups IVB, VB, VIB, VIIB, and be the same or different selected from the ele-

nuclear, binuclear, triauclear, or tetranuclear complex with the provise that formula I can represent a monocompound comprising No. Manb. Manbye, or whithfield respectively with their attendent ligands, L;

- each capable of contributing two to tuelwe T-electrons each Lle, Llb, Llc, and Lld represents none, or 1, 2, or 3 ligands centributing welectrons that can be the same unsubstituted acyclic and cyclic unsaturated compound cyclic arquetic and heterocyclic erometic compounds. and groups and substituted and wesubstituted carboor different ligand selected from substituted and to the valence shall of He, He, He, and He. respectively:
- ri-dentate ligands, each donating 2, 4, or 6 the same or different selected from moso-0-electrons to the welence shell of Me, Mb, MC, and tributing an even number of 0-electrons 12c, and 1.2d represents none, or 1 to 6 Hd, respectively: L20, L20, ligends o that can di-. and
 - valence abell of Me, MP, MC, and Md, respectively? ligands contributing one 0-electron each to the Lile, Lib, List, and Lid represents none, 1, or 2

*-electrons to the valence shells of two or more metal represents none, or 1 to 6 bridging ligands containing o-electrons that can be the same or different ligand and cyclic unsaturated compounds and groups and subselected from subotituted and unsubstituted acyclic stituted and unsubstituted carbocyclic aromatic and acting as a bridging ligand contributing 2 to 24 heterocyclic aromatic compounds, each capable of atoms Ma, Mb, HC, or Md simultaneously!

represents none, or 1 to 12 bridging ligands contributing an even number of 0-electrons that can be the same or valence shells of two or more metal atoms $M^{\mu},\ M^{D},\ M^{C},$ different selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 g-electrons to the or md simultaneously;

1, 2, 3, or 4 d-electrons to the valence shells of two represents mone or 1 to 12 bridging ligands contributing or more ental atoms Nº, Nº, N°, or Nº simultaneously? with the provise that the total electronic charge con-

and Le plus the sum of lonic charge on Ma, Mb, Mc, and Md "30, 130, 125, 130, 13c, 13c, 13c, 13d, 12d, 13d, 14, 15, 20 tributed to Me, Mb, MC, and Md by the ligards Lle, Lle, results in a residual set positive charge of e to the complexi

is an integer having a value of 1, 2, or 3, the residual electrical charge of the complex cations

x is a halogen-containing complex anion of a metal or metalloid:

required to neutralize the charge e on the complex f is an integer of I to 3, the number of complex anions C#11001, 0mg.

g, h, j, and it independently are 0 or 1, with at least one in a preferred composition of the invention, the of these theing equal to 1.

1(L7; .0)#100x

salts of the organometallic cation have the formula:

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wherein

Am represents a metal selected from elements of the Periodic Groups IVB, VB, VIB, VIIB, and VIIIB;

selected from the same group of ligands from which $\mathbb{C}^{1.6}$, y-electrons that can be the same or different ligand represents none or 1 to 6 ligands contributing an even ligands from which Lia, Lib, Lic, and Lid ligands of Llb, Lic, and Lld ligands of Pormula I is selected: L' represents none, one or two ligands contributing different ligand selected from the sums group of number of o-electrons that can be the same or Pormula I is selected;

buted to He by L' and L' plus the fonic charge on He results e, f, and X have the same definition as given in Pormula I. In a most preferred composition of the invention. in a residual net positive charge of e to the complex; and with the provise that the total electronic charge contrithe salts of the organometallic cation are movel and have the formula:

1(12) (1.10) 100 +qx

wherein

represents a metal selected from Ct. Mo. M. Mn. No. Po. 8

n6-benzene compounds and gompounds having 2 to 4 fused rings each capable of contributing 3 to 8 "-electrons L9 represents 1 or # ligands contributing 9-electrons that substituted and unsubstituted n3-sliyl, n3-cyclopents compounds swlepted from 16-benzene and substituted can be the samp or different ligand selected from . clenyl, and n7-cyclohegeatrienyl and n6-arometic to the valence shell of MP!

represents none or 1 to 3 ligands contributing an even different ligand selected from carbon monoxide or number of o-electrons that can be the same of

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buted to the by to and the plus the lonic charge on metal MP alto to not residual positive charge of q to the conwith the preview that the total electricic charge contri-

- ta an indeper banding a walue of 1 or 2, the residual per-centaining complex salon selected from electrical charge of the complex cations
- aired to sestralise the charge q on en tenegric horiday a value of 1 or 2, the members of
- L. II. and III are authorism consistive in addition to being stallic cetions having formulas THE 114 enteltin.
 - All Marmes Lie to 1.10 and well know in the art itim estal ergenmetallic concerds.
- sagname the, the, the, east the in Permits Is and an antifacto deb- grange anergiaite, cute- group made II. are gravided by any measured or polynd harding on excessible essecurated group. acts (yang which have ecceetable e-electrons maler unight of the out constitle", its to ment that the compound for has at the tent and 112
- it, as emploised below, that the lighed con bufficiently claim up a motal atom to form a 4-bond joining invisible fitte way than perticles of high earther erre so ey polymeric con ches, e.g., cottifydiatures; etc, er that the empound is tes a hadenstata, o.g., tricalerectoylems as alleas. seie sydrocarben, e.g., enicolos en then the emptached group (including evolution group) is as bearing the emetimented group is coluble in a A ceryl horonos se ceter. o.g., anyl and as an element, e.g., methonels a of form which the accessible compound the measurested group to the metal atom. to themster on on pound. 14. 16 mm

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and beterocyclic arquetic ligands having up to 25 rings and having less than 60 carbon atoms, and up to 10 hetero atoms discetylens, butadiess, 1,2-dimethylacetylens, cyclobutens, scetyless, propyless, methylecetylens, 1-butens, 2-butens, up to 100 carbon atoms and up to 10 hetero atoms selected Illustrative of ligands Lla, Llb, Llc, Lld, and compounds having less than 100 carbon atoms, preferably tetraceme, and substituted and unsubstituted carbocyclic selenium, boron, antimony, tellurium, silicon, germenium, preents, selentum, boron, antimony, tellurium, silicon, beptens, 1-octens, 4-octens, 3,4-dimethyl-3-bezens, and pentene, cyclopentene, bexame, cyclobenese, 1,3-cyclon3-cyclobexadiemyl, w-cyclobeptatriems, w-cyclooctaheradieme, cyclopentadieme, 1,6-cyclobenadieme, cyclo-L' are the linear and cyclic oletinic and acetylenic permanium, and tim, such as, for example, ethylene, from nitrogen, sulfe, oxygen, phosphorus, arsenic, selected from nitrogen, sulfer, oaygen, phosphorus, 1-decemes n3-allyl, n3-pentenyl, norbornadiene,

nf-glucress, nf-asphihalens, nf-esthraces, nf-chrysens n12-paraegelophama, m12-1,4-diphenylbutama, m3-pyrrole, né-pensonasine, né-ségole, né-acridine, né-carbazole, nf-pyrame, n7-cyclohaptatriesyl, n6-triphenylmethens. and in, such as, for example, "5-cyclopentadienyl, n3-thiopiese, n3-futie, n6-pyridine, n6-y-picoline, 16-benzone, n6-mestiglese, n6-bezzeethylbenzene, na-quinaldine, na-banaopyran, na-thiochrone,

bearene, n6-2,4,6-triphenylphosphehenzene, n5-selenophene, suitable prometic compounds can be found by consulting any q-triphemylems, n'-Bilabensems, n'-arsabensene, n'-stiban6-dibensestannepint, n5-tellusephene, n6-phenothiarsine, n6-selenasthrene, n6-phenotaphosphine, n6-phenarasuine, n6-phonatelluratine, and n6-1-phanylborabentene. Other of many chemical handbooks. As mentioned before, the ligand can be a unit of a polymer, for example the phenyl group in polystyrens. poly(styrene-cobutations), poly(styrene-comethy) math-

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sering a unight overage molecular weight up to 1,000,000 or can be used. It is preferable that 5 to 50 percent of the emetamented or acumatic groups present in the polymer mandeninglantations), poly(n4-cyclopentations); the scrylatel. pely(s-methylatyrene); polyvinylcarbasole, and polymethylphenylailonens; the cyclopentadions group in gridin gram in poly(vinylpyridine), etc. Polymers of with motallic cations.

as to enterticated by groups that do not interfere with th. on the ambability of the ligand to the extent that men of the ligands tle, tlb, tlc, tld, and t? citing of the Masne with the metal atom or which do acting with the metal atom does not take place.

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ich en mathylmoscapto (thiomethouy), phemylmercapto include hydrocarbyl groups such as methyl, 1. matyl, dedacyl, tetracosasyl; phosyl, bentyl, allyl ententen, entinony, tellurium, silicon, permenium chary, butany, and phenoxy; hydrocarbylmercapto mil. and ethymils hydrocarbylony groups ies of embettacking groups, all of which preferably hear then 30 carbon atoms and up to 10 hetero atoms chylosycathonyl such as methosythat free attrages, sulfur, ourges, phosphorus,

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acetyle and beneatly hydrocarbylearbonylony such as emplotibles trimethylgernams tributy ego and cyclebezascarbonylony; bydrocarbyl-144. o.g., acetaride, tresenidos asos boryls helo. peachosyl: hydrocarbylcarbonyl such as m. tada, trues, and fluoro, bydrony; eyano; to, and dimethylaminos diphosylphosphino, and ridge and an baseo, cyclopentas nephtho, is tias anthylecless; othylcollaro; and trimethylolloxy; stens, elen

and the, the, the, and the to remain I, and tata compounds professibly containing up to about 10 earbon L' 15 Formule II and provided by monodentate and polydenetors and up to 10 hetaeo atoms selected from altrogen

methylidens, ethylidens; suitable polydentate compounds or sulfur, oxygen, phosphorus, arsenic, selenium, antimony, compounds of Group VA elements such as amonie, phosphim compounds preferably forming with the metal, Mª, Mb, MC, and tellurium, in addition to the metal atom, following Examples of suitable monodentate comtributylphosphite, isonitriles such as phenyliaunitrile ethanol, butanol, and phenols nitrosculum (1.e., NO*): 1,2-bis(diphenylarsino)ethans, bis(diphenylphosphino)butyliscaitrile; carbene groups such as ethomymothyltriphenylphosphine, triphenylersine, triphenylstibine, pounds or groups are carbon monoxide, carbon sulfide, loss of sero, one, or two hydrogens, the polydentate carbon selenide, carbon telluride, alcohole such as carbene, dithiomethoxycarbame; alkylidemes such as trimethylamine, trimethylphosphine, triphenylamine, diethylemetriamine, 1,3-diisocyanatopropame, and Hd, and HM, a 4-, 5-, or 6-membered saturated or groups include 1,2-bis(diphenylphosphinolethane, methans, ethylenediamine, propylenediamine, unsaturated ring.

oxime. Other suitable groups are the inorganic groups such hydridotripyrazolylberate: the hydroxycarboxylic acids such se 2.4-pentanediones hydroxyhetones such as 2-hydroxyacetobis(perfluoromethyl)-1,2-dithiolene: aminocarboxylic acids phenones a-hydroxygmines such as salicyladoxine; hetoxines se glycollic acid, lactic acid, salicylic acid; polyhydric bouylic dismides such as oxalemide, biurets direcones such se, for example, CBT, SCHT, PT, OHT, ('1", Br . I', and HT such as benail oxime; and glycaimes such as dimethylglysuch as alanine, glycine and oraninobennoic acidi dicarr carbamte, dibenzyldithiocarbamete: xanthates such as et hydroxyamines such as ethanolamine, propanolamine, and phenols such as catechol and 2,2'-dihydromybiphenyl: by, etc. As mentioned belote, the 2-aminophenol; dithiocarbametes such as diethyldithioand the organic grigups such as, for example, acctoay, manthate, phenyl manthater the dithiolenes such as formylony, benzuyle 2 2 2

hered electron. Buitable groups can contain any es them 30 carbon stoms and up to 10 hetero stoms termine I include any group having in its etructure an atom carbon atoms and betaro atoms but preferably Buttable regions the, Lb, Lsc, and Lbd in d from editrogen, seaffer, caygen, phosphorus,

aligh, butangl, epclobensagl; the hydrocarbyl derivacalgl, etc.; manaturated hydrocarbyl groups such a sleader, actioner, tellurium, silicon, germanium of a Group I'M alonest such as trinethylgerneatien, beren. Enuples of such groups are hydrocarbyl and an emethyl, other, propyl, baryl, dodecyl,

wittin, and trimethylallyl, etc.; and organic groups es facuel. acatyl, proplomyl, acryloyl, octadecoyl, teluencedforpl, exelyl, melonyl, o-phtheloyl.

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grang, auch as as acetylesic, -CEC- group of the total melecular weight of the compo or polymerts sergent baving an accessible Edgend Ed to Permits I to provided by any e gramp which have accessable a-electrons

Th-cyclomogratriams, af-egcleoctatetraces, and substituted . 3-cycloberations, cyclopentations, and 1,6-cycloberation and the, much so for example, scotylene, methyl 9-allyl, 99-percentl, normornations, p5-cyclobenationsl, cotylese, discotylese, betedless, 1,2-discthylacetyless, Liyands having up to 25 sings and up to 100 carbon atoms and unsubstituted carbodyclic and heterocyclic aronalis unds professibly baving Ellenterative of ligned L4 are the linear and ores, setimeny, tellurius, silloos, then 60 captur otoms and up to 10 betero atoms m. sulfur, caypes, phosphorus, diene and executante on t. melenskin, b ed form military

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ne-arasbenzene, nedatibabenzane, ne-2,4,6-triphenylphosphabensene, n3-selencimene, n6-dibenzostannepine, n5-telluron6-1-phenylborabengone. Other suitable aromatic cumpounds can be found by consulting any of many chemical handbooks. and up to 10 hetero atoms selected from nitrugen, sulfur, (7,8,9,10,10a,10b)chrysene, n⁶-triphenylene, n⁶, n^{6,-}-peraphene, n6-phenothigraine, n6-selenanthrene, n6-phenoxaoxygen, phosphorus, ersenic, selenium, boron, antimony, example, n5-cyclopentadienyl, n6-benzene, n6-mesitylene né-bensopyran, né-thiochrome, né-benzozazine, né-indole trienyl, m-triphenylmethame, n5-pyrrole, n5-thiophene cyclophane, n6, n6'-1,4-diphenylbutane, n6-silabenzene, tellurium, silicon, germanium, and tin, such as, for n6-anthracene, n6-chrysene, n6-pyrene, n7-cycloheptaphosphine, n6-phenarsarine, n6-phenatellurarine, and n5-furan, n6-pyridine, n6- -picoline, n6-quinaldine, n6-hexamethylbenzene, n6-fluorene, n6-naphthalene, n6-acridine, n6-carbazole, n6-(1,2,3,4,4a,12a)-n6-

solubility of the figand to the extent that complexing with such as methylmerempto (thismethoxy), phenylmercapto (thioacetony, benzoxy, and cyclobenamecarbonylony; hydrocarbylserbonanido, e.g., ecetanido, benzamido: azur buryli halo. dodecyl, tetracoschyl, phemyl, benzyl, allyl, benzylidene. the metal atom dost not take place. Examples of substituting groups, all of which preferably have less than 30 phenoxy): hydrocathyloxycathenyl such as methoxycarbonyl ad phenomy: hydrocarbylmercapto uroups and phenomycarbonyl: hydrocarbylcarwonyl such as formyl, antimony, tellurism, silicon, germanium, tin, and boron, include hydrocarbys groups buch as methyl, ethyl, butyl, nitrugen, sulfur, emygen, phosphorus, arsenic, selenium, groups that do not interiers with the complexing of the Each of the ligands L⁴ can be substituted by ligand with the megal atom or which do not reduce the carbon atoms and up to 10 betero atoms selected from acetyl, and benaogl: hydrogarbylcarbonylesy such as ethenyl, and ethyaple hydroserbyloxy groups such as mathoxy, butoxy.

condensed rings such as benso, cyclopenta; asphtho, indeno; dighemylarainos diphemylatibines trimethylgermanes tributyl ..g., chloro, todo, bremo, and fluoro, hydroxy; cyano; nitro: mitromo, oncy dimethylaminos diphenylphosphino, ties methyleelenos ethyltelluros and trimethyleilonys I the like.

atems and up to 10 betero etoms selected from altropes, sul Ligand L^S is provided by monodestate and polydentate compounds preferably containing up to about 30 carbon elimitem. Europios of pultable unachentate empounds or mr. orygen, phosphores, erosale, selenium, astimony, and Merido, estber tellurido, elechols such as ethansi, De ere certen noentide, earten sulfide, cartes

payliseeterile; suitable polydentate compounds or not, and phonelly mittroscation (1.e., not); compounds of hime, trimbanylandian, trippenylatibine, iscaltriles me taches 1.3-cisisiphosylphosphinolothem, 1,3-bisinclementation, proppionedianine, dicthylesetrianine, Wlessine bethere, bis (dipherylphosphine lasthese, o W. elements Outh as tripbonylemies, tripbonyle

equarterylic neith such as phoculic seid, lactic seid, 1.3-dilangeantographes, and hydridetripyrasolylbecates the 1.2'-dibytomintaningia fathranestee each as ethenise, selfertie selds polytyfrie Shenole such as catechal and

pendentes, and Designable dichlocarbenates such as dischyldithlocatherein, dibenyldithlocatheres mathates bouyild seids such as alseles, glycias and o-seincheagold men as other smetheter plany 1 manthates the dithiolones ch as biefprefluoremethyl)-1,2-dithialems animearscids dicertorylis dismides such as oralamide, bluret,

disectores and as 2,4-perioandieses hydroxytetones such as doctors technisms duch as bearit oxines and glyoxines such gaste groups such as, the example, Or", SON", F", OH", C1" as dissethylglycating. Other saittable groups are the incrmanes 4-hydronypuides such as salleyle-Br", 1", and W" and the organic groups such as, for example, ecetory, termylogy, beatoyloxy, etc.

Suitable radical Lo in Formula I includes any unpaired electrons. Suitable groups can contain any number ersenic, selenium, antimony, tellurium, silicon, germanium tin, and boron. Examples of such groups are hydrocarby. of carbon atoms and hetero atoms but preferably contain group having in its structure an atom with two or more groups such as methenyl, ethenyl, propenyl, heaenyl, less than 30 carbon atoms and up to 10 hetero atoms selected from mitrogen, sulfur, oxygen, phosphorus,

Suitable anions, X, in Pormulas I and II, of uso as the counteries in the ionic saits of the organometallic complex cation to the proferred radiation-sensitive compositions of the invention are those in which I has the

dodecenyl, methingl, and carbide.

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preferably are boron, aluminum, antimony, tin, arsenic, and phosphorus. Preferably, the halogen, O, of Formula II, is formula DOr, wherein D is a metal from Groups IB to VIIIS Periodic Chart of Elements, 0 is a helogen atom, and r is metals are copper, sinc, titanium, vanadium, chromium, an integer having a value of 1 to 6. Preferably, the or a metal or metalloid from Groups IIIA to VA of the manganese, irod, cobalt, or nickel and the metalloids

tion on exposure to energy than are salts having other anions. of the organometallic complex salts having these three anions invention that are relatively more active toward polymerisaare novel and all of these salts provide compositions of the preferably, the anions are As76, Sbf6, and Sbf508. Some are Bril. Pfg. Sbrg., Sbrgowl, Asfg., and SbClg., Host GaCld, Inf., Tife, Inf., etc. Preferably, the anions BF4", PF6", Aaf6", SbF6", Pecl4", Sacl5", SbF5", AlF6", 2

chlorine or fluorine. Illustrative of suitable anions are

and cyclic oletinic compounds formally described as having saturated carbon and heeing less than 10 carbon atoms and no heterostoms, such as for example n3-allyl, n3-butenyl, Ligand L9 in Permula III is provided by linear lost a hydride or a proton alpha to a double bond from a n3-pentenyl, n3-hexenyl, n3-heptenyl, n3-octenyl, 5

methoxy, ethoxy, hydroxy, nitro, chloro, brome, anthee, and

M. M-dimethylamino on the phenyl ring in the 2,3; 2,4; or

There are restrictions on the total aum of

3,4 positions.

different and ctud from methyl, ethyl, propyl, impropyll,

n7-cyclobeptatrienyl ligand may be formally described as an nf-carbasole, nf-biphenyl, nf-triphenylene, nf-naphthalene and up to 24 carbon atoms and up to 2 heteroatoms selected meing understood that both the n5-cyclopentadienyl and the arometic ligand) and aromatic ligands having up to 4 rings "-diphenyl amine, ne-diphenylmethane, ne-triphenylmethan m-anthracene, m-phenanthracene, n6-pyrene, n6-chrysene, n3-nomenyl, n3-decenyl, n3-cyclobutenyl, n3-cyclopentenyl, diesyl, n5-cyclohexadienyl, and n7-cycloheptatrienyl (it bensens (durene), n6-pentamethylbensene, n6-hexamethylfrom nitrogen, oxygen, and sulfur, such as, for example q6-1,2,3,5-tetramethylbenzene, n6-1,2,4,5-tetramethylnl-cyclonomenyl, nl-cyclodecenyl, n5-methylcyclopentadienyl, n5-cyclopentadienyl, n5-pentamethylcyclopentafe-chlorobensene, ne-bromobensene, ne-fluorobensene, "-thiosnisole, n6-aniline, n6-M, M-dimethylaniline, n3-cyclobezenyl, n3-cyclobeptenyl, n3-cyclooctenyl, we-o-rylene, n6-p-xylene, n6-1,3,5-trimethylbensene mesitylenel, n6-1,2,4-trimethylbensene, n6-1,3,5ne-toluene, ne-ethylbenzene, ne-isopropylbenzene, nf-propylbenzene, n6-t-butylbenzene, n6-m-xylene, meterralin, ne-ethoxybensene, ne-benzoic acid, triisopylbenzene, n6-1,2,3,4-tetramethylbenzene, me-cyanobenzene, ne-nitrobenzene, ne-fluorene, benzene, ne-phenol, ne-thiophenol, ne-anisole,

III in which complexed metal we, we, we, we sad we have is eighteen. Those skilled in the art, however, hane that metallic compounds tend to be those compounds in which the sum of the electrons domated by the ligands and the metal governed by the "eighteen electron rule" isos <u>J. Chem. Md.</u> there are exceptions to this rule and that organizatellic 16, 811 (1969)]. This rule is sometimes called the "nine metal-metal banding are described by Formulas I, II, and involving intramolecular metal-metal bonding, this sum is orbital rule", "the effective number rule", or the "rate and the valence electrons possessed by the metal, HP, AP gas rule". This rule states that the most stable organ organometallic complex cations not including intramole complex compounds having a sum of 16, 17, 19, and 20 a total sum of 16, 17, 18, 19, or 20 electrons in the electrons are also known. Therefore, ionic salts of I, L' and L⁹ of Pormela II, and L⁹ and L¹⁰ of Pormula valence shell and a regidual net pesitive charge of electrons donated by the ligands, the, the, the, the [36, 21c, 12c, 13c, 13d, 12d, 13d, 14, 15 and 16 of 1 HC, Hd, HP, and HP. For most complex compounds not 3 are included within the scope of the invention. 2

which intranslation matal-metal bending entate serious departure from the "eighteen electron rule" can occur. It has been proposed [J. Meet. Them. 90c. 100, 5305 (1878)] the departure from the "eigiteen electron rule" in these transition metal complemes is due to the metal metal complemes is due to the metal metal electrons around each metal bending. Hence, rather than count electrons around each metal separately in a metal cluster, cluster valence electron. (CVE) are counted. A dinuclear complex, metal to

nl2-paracyclophane, nl2-1,4-diphenylbutane, poly(n⁶-atyrene)

poly(n0-m-vinylearbasole), poly(n6-methylphenylsilozane),

(n6-1,2,3,4,4a,9a)-9-(phenylmethylidene)fluorene, and

ligands may be disubstituted by groups that may be some or

methylaming on the phenyl ring. Also, the latter two

ethony, hydrony, nitro, chloro, brono, amino, and M.M-di-

selected from methyl, ethyl, propyl, isopropyl, methoxy,

(n6-1,2,3,4,4a,9a)-9-(3-phenyl-2-propenylidene)fluorene. The latter two ligands may be mono-substituted by groups

ns-quincitie, ns-isoquincline, ns-indole, ns-benzimidazole,

me-1,2-benzopyrazole, ne-benzothiazole, ne-benzozazole,

me-indan, ne-peracyclophane, ne-1,4-diphenylbutane,

Hamphe, or whyblish has a total sum of 345 42, 44, 46, 48, nave 34 CVEs, a trinuclear complex, Manbac, 48 CVEs, and a tetranuclear organometallic complex cations are described butterfly, and aquare planar geometry is seen to have 60. trinuclear complex and 58 CVEs for a tetranuclear complex by Pormule 1 in which the complexed metal cluster, Manb. trooly, and a residual not positive charge of 1, 2, or 3 50; or 58, 60, 67, 64 CVEs in the valence shell, respechowever, know that there are exceptions to this electron 62, or 64 CVEs, respectively. Those skilled in the art. counting method and that organometallic complex cluster are also known. Therefore, foric salts of di, tri, or compounds having a sum of 42, 44, 46, 50 CVEs for a tetranuclear complex, Mambhend, having tetrahedron, are included within the acope of this invention.

described by Pormulas I, II, III of use in the compositions of the invention are those selts that upon application of cationic polymeritation. The level of cationic activity will, of course, depend on the choice of metal, ligands, radistion having a wavelength from about 200 to 600 mm, will generate an active species capable of initiating Suitable organometallic complex tonic salts sufficient energy, either thermal or electromagnetic and counterions in the salt.

an intermodiate strength mucleophile such as substituted or procedures used to determine it a particular compound will to minists cationic polymerization are those that will add unsubstituted trialkyl- and triarylphosphines (preferably Suitable tonic salts that are activated by heat pyridines, and anilines. Examples of such compounds are lons' 5, Chapter 37, 1976, diley-interscience, Hew York. described in Tetrahedron 16, 3047 (1978) and "Carbonium erighenylphosphine), trialkyl- and triarylphosphites, These reviews contain references to the experimental add such a nucleophile.

electricasquetic radiation to initiate cationic polymeriza-Suitable ionic salts that are activeled by

coordination site on the metal. The ability to liberate at least one coordination site upon photolysis can be werlfied by doing a ligand exchange experiment. In such an experition are those that upon photolysis liberate at least one ment, the compound

⁻⁽[अर्थन्ता(ज्या)(ज्या)^वविश्वव्या(क्या)(व्या)^व(आक्रा)(क्या)(व्या) 3x -,(g))(5))(g)) (pH(p(1)(p2))(p(1))

rigorous mathod would havelwe isolation of the photographot length, irrediation time. Hight source. Hight source intermentalist for the particular system under study. Stamples ligands is carbon memoxide, them infrared apectroscopy in a ment whould be carried out. A.s. organometallic tonic soit ligand concentration, choice of solvent, izradiation wave-10 indeed added or exchanged with at least one ligand Li to L⁶ ber which the ligand exchange experijolysis can be compared with that taken technique such as attendental assity to the L bos after completion of the reaction and use of an analytion. concentration, identily of the entering ligand, entering analysis technique, etc. must be adjusted by the experiof Formula I can be determined by any number of analytical monitor the reaction before, during, and after photolysis. Ocherated of the conditions which have been used to study ligand sity, reaction vessel, presence or absence of ouygen. 2 pordination appere of the metal. ligand L (L.can be pt the L² or L² types). That L has If L or at least one of the List, Litt, List, or List eschange reactions are contained in "Organization after completion of the reaction to determine if the is photolyzed in the presence of a potential entering determination to use some appetroacopic technique to techniques. It is particularly convenient for this suspected ligand substituted product is present. UV/visible or MR apectroscopy can be employed. well suited technique to monitor the reaction. spectrum before phot Indeed entered the profer conditions w 2 2

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references therein, and in Inorg. Chem., 19, 3007 (1960). Photochemistry", 1979, Academic Press, New York, and

complex cations useful in the composition of the invention include the following (proposed structures of typical com-Examples of suitable salts of organometallic pounds are shown at the end of the list):

(n5-cyclopentadienyl)tricarbonyliron(1+) hexafluorophosphate(a).

("5-cyclopentadienyl)dicarbonylthiocarbonyliron(1+) cetrafluoroborate 9

(n2-cyclopentadienyl)carbonylbis(triphenylstibine)iron(l+) hexaf l vorophosphate

(n?-cyclopentadienyl)tricarbonylruthenium(1+)

tetrachloroferrate

(n5-cyclopentadienyl)dicarbonyltriphenylstibineiron(l+)

?

-ethylcyclopentadienylldicarbonylnitrosylmanganese(1+) hemafluoroantimonate(b) hexafluoroantimonate Ė

-sethylcyclopentationyl) (\mathfrak{n}^{3} -ellyl)dicarbonylmanganese (1+) tetrafluoroborate(C) £

195-cyclopentadienyl)tetracarbonylmolybdenum(1+)

hexafluorophosphete

(72-cyclobexadienyl)tricarbonylirun(1+) hexafluoroarsenate(d) (45-pentadienyl)tricarbonyliron(1+) tetrafluoroborate [n5-cyclobexodienyl](etbylidene)carbonyltriphenyl-

phosphinairon(1+) tetrafluoroborate

(n2-cyclopentadienyl)(ethoxymethylcarbene)carbonyltriphenylphosphingiron(1+) tetrafluoroborate

(r 5-cyclopentadienyl)(dithiomethoxycarbene)dicarbonyliron(1+) nexafluorophosphate

9

-cyclopencedingyl)dicarbonylmethylisonitrileiron(l+) he kaf luoroar senate Dis(F5-cyclopentadienyl)(F2-ethylene)(G-methyl)tungsten(l+) nexafluorophosphate

in6-toluene) tricar bony lmangansse (1+) hexafluoroantimonate(w)

of mesitylencitricarbonylrhenium(1.) hemafluorcantimonate

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(n7-cycloheptatrienyl)tricarbonylchromium(l+)

hexafluorophosphate

(n7-cycloheptatrienyl)tricarbonyltungaten(1+) hexafluoroarsenate(f)

(n^5 -cyclopentadienyl) (n^2 -l-pentene) dicarbomyliron(1+) tetrafluoroborate

(n6-benzene)(n5-cyclopentadienyl)iron(1+)

(n6-mesitylene)(n5-cyclopentadienyl)iron(1+) hexafluorophosphate.

tetrafluoroborate

(n6-maphthalene)(n5-cyclopentadienyl)iron(1+)

(n6-acetophenoms)(n5-methylcyclopentadienyl)iron(1+) hexaflucroentimonate reenate hexafluor

edienyl)cebalt(1+) hemeflworophosphate iadienyl)iron(1+) hexafluoroantimomate bis(n5-chlorocyglopentadienyl)nickel(l+) hexafluorop bis(n5-cyclopen bis(n2-cyclopen 2

bis(n6-hexameta 1benzune) mickel(2+) hexafluoroantimonate bis(n6-hexamethelbenzene)cobalt(2+) benafluoroarsenate phenylphosphinecobalt(1+) hexafluorobis(n6-benzene) hrcmium(1+) hemafluoroantimonate(9) tatracarbonyltm 20

riphenylyhosphine)iridium(1+) hensiluorotricarbonylbis phosphate

phosphate

lbenzen**ejhe**ngenese(1+) tetrafluoroborate rosylmolybdenum(1+) benefluorophosphate proposition (1+) tetrafluoroborate arbonylimm(1.) hemafluoroantimonate e)iros(20) hexatluorosatimonete(h) e)vanadigm(1+) hexafluorophosphate lum(1+) beastluoroentimonate bisin6-mesityle pentacarbonyla hexacarbonylrh (n3-ellyl)pente (n3-ellyl)tetr bis (no-hexamet 52 2

tenyl)(macyclopentadienyl)manganese(l+) renyl)(-cyclopentedienyl) cnromium(1.) respete (nº-cyclooctate Die(no-mesity) (n'-cyclohepta head () uo

-cyclopent 'senyl) iron(1+) nexalluoro-Soaphate phosphate (1) | up-{}norene) (| hexaf luor 2

(1,6-1-phenylborabenzene)(n5-cyclopentagrenyl)cobalt(1+) hexafluorophosphate

-cyclopentadienyl)(n5-N-methylpyrrolyl)iron(1+)

5 (nº-2, 3, 4,5-tet: athiomethoxybenzene) (n5-cyclopentadienyl)iron(1+) hexafluoroarsenate hexafluorophosphate

[(46-1,2,3,4,5,6)(46-7,8,9,10,11,12)biphenyl]bis(15-cyclopentadienyl)difron(2+) tetrafluoroborate

{ (q6-1,2,3,4,4a,9a) (n6-5,6,7,8,8a,5a) fluorene] bis(n⁵-cyclopentadienyl)diiron(2+) hexafluorophosphate

[(n6-1,2,3,4,4a,9a)(n6-5,6,7,8,8a,5a)fluorene]Dis-

(n6-benzene)diiron(4+) hexafluorophosphate

bis(n6-benzene)dichromium(2+) hexafluoroantimonate [(46-1,2,3,4,4a,12a)(n6-7,8,9,10,10a,6a)chrysene]-

dicarbony 1 (bis (dipheny lphosphino) ethans) bis (n⁵-cyclopentatetra((n5-cyclopentadienyl)carbonyliron)(1+) hexafluorodienyl)diiron(1+) hexafluorophosphate

tris[(n6-bonzene)cobalt]dicarbonyl(1+) hexafluorophosphate phosphate

14a,10o,10n,12a)(n⁶-18t,18u,10v,18v,18x,18y)-tripyreno 2-,1-,16-,9-,8-,7--xysa,b,c.d(trinaphthalene)tetra(n⁵eris(n5-cyclopentadienyl)dinichel(1+) hexafluorophosphato [(#-1,2,29,18c;18b,18a)(n6-7,8,8a;18i,18h,7a)(n6-13,14,-(2,1,10,9,0,7-defghij:2',1',10',9',8',7'-nopgret:

-4,5,5a,28c,78b,3a)(n6-8a,8b,20d,22a,22b,24c)-18,14H-4,5,6;6",5",10":4",5",6")diisoquino(2,1-a:2",1"-a¹)dipyrano(3,4,5, gh: 3',4',5'-g'h')anthra(2',1',9': cyclopentadiesyl)tetrairon(4+) hexafluoroantimonte diperimidine|bis(n5-cyclopentadienyl)difron(2+)

[(n6-1,2,3,3s,13b,13e)beaso(10,11)chryseno(2,3-d)(1,3)diomolej (n5-methylcyclopentadienyl) iron(1+) hexafluor cantimonate hexafluorophosphate

. acetylcyclopentadienyl)difrom(2+) tetrafluorobofale Dis(12-acetylcyclopestadienyl)iros(1+) tetrafluoroborato (1;2,3,4-defi5,6,7,8-d'e's')diphenanthrenelbis(n⁵-[176-1,2,3,3e,16c,16b][n6-9,10,11,11a,13c,8b)cycloocta-

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32e, 32b, 29e) naphth(0',1',2':6,5,10) enthre(2,3-1) naphth-(2111,31111611,711)Indolo(2",315'6')naphth(2'3'14,5)indolo(2,3-g)naphtho(2,3-i')benzo(1,2-a:4,5-a')dicar-[[n6-1,2,2,4,4a,42a][n6-16,17,18,19,19a,15a][n6-30,31,32, bazole)tris(n5-cyclopentadienyl)triiron(3+) hexa-

(n3-1,3-dimethyl-allyl)tricarbonyliron(*1) bexachloro-(13-1-methyl-allyl)tricarbonyliron(+1) hexafluorophos fluoroantimonate

10 [(n5-cyclopentadienyl)nichelmonacarbonyltricobalt[(+1)] hexafluorophosphate antimonate

Di-(w-carbonyltricarbonyl)(dicarbonyliros)(bewacarbonylhydrodiruthenium)-y-hydro-osmium(2Pe-hu)(Po-Os)-(20s-Ru)(Ru-Ru)(+1) hexafluorophosphate⁽¹⁾ Tetra-p-hydrotetrakis((1,2,3,4,5-q)-1,2,3,4,5-pentamothyl-2, 4-cyclopentadienyl-1-yll-tetra-tetrahedry-rhodium-(+2) bis(hexafluorophosphate)(h)

2

carbonyliron)rhodium(2Dh-Pe)(+1) hexafluorophosphate(1) Bis(v-diphenylphosphido-p-carbonyl-s-methylcyclopentadienyl-

Di-#-carbonylpentacarbonyl-w-carbonyldi-W-cyclopentadienyldirhodio)diiron(fe-fe)(4fe-fh)(fh-fh)(+1) hexafluoroersenate(B) 2

Di-#3-carbonyltricarbonylbis(s-cyclopentadienylmichello)iron(27e-Mi)(Mi-Mi)(+1) bunafluoroantimonata(n)

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alkyll, R' is hydrocarbyl, hydrocarbylcarbonyl, helosydrocarbyl, or hydroayhydrocarbyl when X is oargen, or R' is where X is -0- or -MR"-- (where R" is hydrogen or lower

alkaryl, arylalkyl, and the like. In general, mondmers of this type contain a vinyl group and are typicied by vinyl hydrocarbyl, hydrocarbylcarbonyl, or hydrocarbylaulfonyl other hydrocarbyl, or R' (as hydrocarbylcarbonyl) and R' when X is nitrogen, and Y is hydrogen, alkyl, aryl, or ether, vinyl arbutyl ether, vinyl 2-chloroethyl ether, ally) others, such as vinyl methyl other, vinyl othyl mean alkyl, altenyl, eryl, cycloshkyl, cycloshenyl, i cucture containing nitrogen as a betero ring atom. term "hydrocarbyl" is used herein in its usual sense can be c ... sected to form a 5- or 6-membered cyclic 2

of from 1 to 6, preferably 1 to 3. Perticularly upoful and

the alignments, eyclosliphents, and glycidyl other type

recyclic and will typically have an apary equivalency

bey can be allehette, cyclosliphetic, econetic, or

echern are the m

meric and polymeric types of epoxides

mages, mercel Bether, Inc. (1969). Suitable 1,2-cyclic

a. plyciagi other of bisphenel A. 3, 4-epoxycyclobenylaethyl

mecarbonylete, 3.4-spony-6-methylcyclo-

pary-6-mathyleyclobenamecarbonylate.

may lesetay 1-3, 4-a

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and the last

Houses, glycidol, butadione oxide, glycidyl methocrylate.

syress exists, winyleyelohouses onide, winyleyelohouses

1.3-months such as propylene oxide, epichlorohydrin,

octamesulfommuide and H-vinylpyrrolidone. A description of butyl ether, and H-vinyl compounds such as H-vinyl-H-me'hyl winyl monumers and their use in propering polymers is set 2-ethylhesyl other, vingl ethers of substituted alighatic alcohols such as 1,4-di(ethenoxy)batene, vinyl 4-hydroxyforth in "Vinyl and Related Polymers." by Schildknecht. published by John Miley's Sons, Inc., New York (1952). vinyl isobutyl ether, vinyl phenyl ether and vinyl

Other cationisally-sessitive monomers which can be polymerized in this invention include ethylenically unmakurated hydrocarbons such as techutylens, 1,3-buta-2-vingl-1,3-dioxolane and 2-methad-1,3-dioxolane; and diese, incpreme, styress, and diwinglbenrenes cyclic formals such as trioxams, 1.3-diesolane.

thesthylationses hering cyclosliphetic epoxide or glycidyl

digiyeidyl other, and opcay allicense, e.g.,

.e-becameted digitated other, polyplycidyl other of maifementifetyth resease or sevolet reals, resorcised

layelegemendiame dianide, aparidized polybutediame,

eny-6-mothyleyelohenylmethylledipote,

cher graups. A other meriaty of commercial openy recina

enalted and listed to "Resident of they belos" by and Sevilla, appress 8611 Sect Company, New York (1967) Aspessmentition of the 1.3-

to "thung facta technology" by P. F. Bruins, John

course which can be polymerized in eccordance with this

invention to copresented by the general formulas

anceaer angles class of estimates systemative

3,3-bis(chicomethyl)emetems, and tetrahydrofurms.

accordance with this impaction are onstant.

and 1,4-cyclic others which can be polymerised in

1130y 6 Soms, May Year (1968).

redical, a garboxy-containing hydrocarbon radical or ester cyclic silosanes which can contain various groups attached group, a cyanohydrocarbon radicate, hydrogen, halogen or a to the silicon atom such as a hydrocarbon radical (alkyl, allyl or acryloylouy-albyl), a halogenated hydrocarbon aryl, elharyll, an elhenyl nydromerbon reducal (vinyl. hydrony group. Representative opelic siloxanes are 2

ethylemically unmaintained hydrocarbons, cyclic formuls, and

1,3-, and 1,4-eponides), vinyl others, M-vinyl compounds,

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cyclic organisations. In extensive list of cationically

polymerizable manners which can be used in this invention

220 gives in U.S. Petest Bos. 3,347,676 and 3,842,019.

see with this assertion include those described in

maing Polymerisetions", Vol. 2, by Princh and

The cyclic ethers which can be polymerized in

phonylhaptamethylcyclotetrasilouane, vinylheptamethylcyclochloruprogramate anothylopolotetrasilonana, 1,2,3-tril(3,3,3tercasilosame, methaciyloylonymethylheptamethylcyclouetraerithmoregrouplitimethiltyclotrisilomans, ac.tompsethylbenemethy leyelotrisilonene, octamethy leyelotetrasilonane eilessne, and chlorchaptamethylcyclotetrasilomans. Othe slogy of Siliconse" by Walter Holl, Academic Press allonems, 2-bromosthylheptamethylcyclotetrasizcusme, 3methylogicletetrasilenses, cyanomethylbeptamethylcycletetresilonese, 1, 2, 3-tribydrotrimethyloyclotriknown excite ellowance are listed in "Chemistry and ack (1968). Tables 41, 44 and 45.

as each as hemmethyldisilonese, chloropentamethyl terninate the granteg chain and provide stable fluids or nos of relatively low molecular weight lisear The cyclic allocanes can also be polymerised Mailerum and oct. methyltrisiloness which serve to thatde haring meetive and groups.

estion. Is perticular, cyclic others which are readily patienically-semaitive monomers which can be used in this mays placings exper, 1,3-button outdo, elgizoidyl other med & to.g., "thos 620" and "DE: 331"), vingl-.de. glyciati, glyciayl methecrylate, octylene oxide, milable include propriess onide, onstant, epichlotofarm, etyrose oxide, visyloyoloheme Ph.-4221'), 3,4-spory-6-metaylcycloberyli sthyl 3,4-Thore to a most of commercially available mycyclobesamecarbonylate (e.g., whether - late

gipcol (e.g., "gal.-4050" and "ERL-1052"), dipentene dionide (e.g., "ER-1269"), aposidized pelybutediese (e.g., "Oniron 2661"1, siliceme epocy (e.g., "fyl-Kem 90"), 1,4-butenediol -gre-42001, alighetic apary meditied with polypropylems diglycidyl other te.p., "Araldica MD-2"), polyglycidyl bis(1,4-apany-6-asthylopelchenylasthylladipets (0.9., server of phemoidocmaldehyde movolak (e.g., "DER-431", 6-methylogelebenomenenthonylate (e.g., "BM-4201"),

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agents, or hardeners which also are well known (see Lee and (e.g., "Koponite"), polyglycol disponide (e.g., "DER 736"), Maville and Bruins, supra). Representative of the co-curmodified epoxide (e.g., "QE3599"), polyfunctional flexible epoxides (e.g., "Plexibiliser 151"), and mixtures thereof. "Epi-Rez 571" and "DEM-418"), resorcinol diglycidyl ether as well as mixtures thereof with co-curatives, Cuting polyacrylate epoxide (e.g., "Epocryl U-14"), urethane

suc. as nadic methyl anhydride, cyclopentanetetracarboxylic atives of hardeners which can be used are acid anhydrides In general, the polymerisation of cationicallydianhydride, pyromellitic anhydride, cis-1,2-cyclohexanedicarbonylic anhydridm, and mintures thereof.

sensitive monomers with the lonic selt of an organometallic majority of cationically-sensitive monomers, although low temperature (e.g., -10°C) or elevated temperatures (e.g., 30° to 200°C; preferably 50° to 150°t;, can be used to complex can be carried out at room temperature for the either subdue the exotherm of polymerization or to

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range of 50° to 250°C, preferably from 50° to 150°C, can be monomer (1.4., a catalytically effective amount) under the fach amount generally will be in 0.5 to 5.0 weight percente and most preferably 1.0 to 2.0 accelerate the polymerization. In the case of latent sait used as a catalyst in this invantion should be sufficient catalysts of this invention, temperatures generally in th the range of about 0.01 to 20 weight percent, preferably to effect polymerization of the cathonically-sensitive organometallic complex to be used. The temperature of polymerization and amount of application of the polymerhed or cured product. The spendent on the particular weight percent, based on the weight of cattonicallyser used and the desired catalyst will wary and be cationically-sensitive mos amount of ionic salt of a desired use conditions. 2

Solvents can be used to assist in dissolution of the tonic salt in the cathenically-senattive material and sensitive monomer.

are preferred for use in the polymerisable compositions. Representative solvents include acetons, methyl ethyl ketone, cyclopentosome, methyl cellosol's acetate, methyleme chloride, aitromethane, methylformete, ecotositrile, and 1,2-dimethosyethese (glyne). The careble or polymerisable compositions of this and the tomic selt of an organizatilic complex as catalyst catalysts such as My or S' . diethyl ether or the radiation maitive only saits are used. Thus, the compositions den evention congrising the outfolioally-sensitive monomerial can be used for applications such as those in which other cettentonly essettive compositions employing levis sold seting and molding compounds, potting and escapeulating se meed as affectives, caulting and sealing compounds, is, impregnating and coating compounds, etc.

illica, tale, glass bubbles, clay, reinforcing fibers, dys pignemes, planticiants, ally opents, anticuidants, surface saifying aparts, etc.,) as long as they do not interfere ntallie complem to mediation-sessitive, absorb men of the composition or, where the imple salt of medition may comtain adjuvants (e.g., fillers, such as d tenic ergenometallic complex used. In addition, the Aing on the particular cationically-sensitive non rich the polymerisacion of the cationically-prasitive catiaties to which the complex is responsive.

deradatet and visible majies of the spectrus (e.g., about upon such factors as the identity and concentration of .no organizatellic faute complex, the particular estionically-For those competitions of the invention which are 188 to 660m) can be used. Suitable sources of radiation mense lange, comblett, etc. The required mount of empendence to effect polymerization is dependent extonically-semitting monomers and an ionic selt of an ediction-engities, 1.6., the compositions containing mealite complex of Pormulas I, II, and III, any rue of entition emitting active radiation is the include mercury supper discharge lamps, carbon arts, angelten lemme,

Optionally, type of substrate, intensity of the radiation source and sensitive monomer, the thickness of the exposed meteriel, it is within the scape of this invention to include specamount of heat associated with the radiation.

(1973), and include pyrane, fluoroanthrene, benzil, chrysene range of 6.01 to 10 parts, and preferably 0.1 to 1.0 parts. Any photosensitizer may be useful if its triplet energy is Handbook of Photochemistry, Marcel Dekher Inc., 87, 27-35 p-terphenyl, aconephthene, rephthelene, phenanthrene, and bighenyl. When present, the amount of sensitizer used in the practice of the present invention is generally in the by weight of sensitiser per part of organometallic salt. tral sensitizers in the radiation-sensitive composition. at least 45 kgal/mole. Examples of such sensitizers are given in Table 2-1 of the reference, Steven L. Murov,

and amounts thereof section in these examples, which are in onsisting of 1 part by weight of winylcyclobenene d 1 part by weight of 3,4-epoxycyclohexylmethyl-The objects and advantages of this invention are syclohexanecarboylete. The particular materials parts by weight, as well as other conditions and datails should not be construed to unduly limit this invention. gire as cationically-sensitive monomer a stock llustrated by the following examples, many of which ut solution 3.4-epox further dioxide

EXAMPLES 1-4.

winylidene chloride primed "5 micrometer polyester using a Polymerizable solutions were prepared by mixing | ===sitylene| (==-cyclopentadienyl) iron(l+) (each prepare number 22 wire wound coating rod and the coatings allowed tively, of (Enample 1) the hexafluoroantimomete, (Example in four maitable vessels 10 parts of stock solution, 1.0 part of acetonitrile, and 0.1 part in each vessel respecphosphate, and (Example 4) the tetrafluoroborate salt of Florida (1978)). The solutions were coated onto polyas described in W. A. Hendrickson, Ph.D. thesis, U. of 2) the hemafluoroaremate, (Guample 3) the hexafluoro-

to air dry for 10 minutes. The coated samples were then exposed to a 150 walt tungsten spoilight at a distance of 10 cm from the sample surface. The time required to produce a non-techy surface for each sample is given in Table I.

TABLE 1

Time to Produce non-tacky surface	30 aec 45 aec 120 aec
	9 9 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
Counterion of (n6-maitylene)(n5-cyclopentadienyl)-	- 24.6 -
6-mesitylene)	
	. n n •

(a) becomes non-tacky after heating at 100°C for 60 min.

EXAMPLES 5-7

Coatings were prepared as described in Examples 1-4 using as catalyst the heasthorophosphate salts of dispersional salts of the salts were prepared according to the procedure described in 3. Organometal. Chem. 101, 221 exposed to the output of the 150 watt tungsten lamp as described in Examples of each coating (labeled (b)) were described in Examples of the 150 watt tungsten lamp as (labeled (c)) were exposed to the output of the 150 watt tungsten lamp that passed through a light filter that produce a non-tacky coating for each sample is recorded in table 11.

1990010

TABLE 11

Time to produce

Ho. hexa	JEATENES		
- _g L)	12	(<u>)</u>	(0)
8			101111 minus 151111
		2	99 990
- ()	(n ⁶ -chrysene)(n ⁵ -cyclopenta- dlenyl)tron(1+)		
4		ບ ຈ ອ ຄຽ	3
7	(n'-pyrene)(n2-cyclepente- dienyl)iron(l+)	15 866	2 2

EXAMPLES & and 9

The procedure of Example 3-7 was repeated using an initial set the hexafluorophosphate selt and the hexafluorophosphate selt and the hexafluorophosphate in the cyclopentadiasy).

iron(1+). The time required to produce a non-tanky surface with the hexafluorophosphate salt use 60 accomes for expensers without the filter and 120 seconds with the filter.

With the hexafluoroantimesate salt, exposures to produce a non-tacky surface were 10 and 60 seconds respectively.

The (n⁶-fluoreme)(n⁵-cyclopentadiomyl)igne(1+) salts were prepared as described in Mendrichaes, Fn.D. thesis, Univ. of Plorids (1978).

EXAMPLES 10-15

parts of stock solution, 2 parts of sectore and 0.1 part of each of the various organizatellis complex salts shown in Table iII. Each solution was coated and dried as described in Examples 1-4 and exposed as described in Examples 5-7.

The time required to produce a non-tacky surface for each is given in Table III.

Time to produce non-

100-1,2,3,4,40,90)-9-(4-methony-	metrylidene)flucrems}- (***-cyclopentadien;!)iron(1+)	10 [(16-1,2,3,4,4e,9e)(-methylatany)-	NO.	ns filler 440m filter
----------------------------------	--	---------------------------------------	-----	-----------------------

[116-1,2,1,4,40,30]-9-(2,4-dimetrony-

|--|

	٠.	
		3
(m6-1,2,3,4,40,90)-9-(3-pteny1-2-	-) iron(1+)
. 3. 4. 4a. 9a) -	rupery lidene) fluccene	-cyclopentedieny)) iron
[m _{6-1,2}	property	M3-CF
=		

EXAMPLE 16

Ph.D. Thesis of M. A. Mendrichson), was coated and dried as A coating solution, prepared by mixing 13 parts of stock solution, I part of acetomitrile and 0.1 part of phosphate, (prepared as described in the previously cited seconds were required to produce a non-tacky surface when the coating was exposed to the output of a 275 watt G.E. (n6-toluene)(n5-cyclopemtadienyl)iron(i+) hexaflu-ronon-tacky surface was obtained in 60 seconds. Only 30 10 described in Examples 1-4. On exposure of the dried coating to a 150 watt tungsten spotlight at 10 cm, a 15 sunlamp at 10 cm.

EXAMPLES 17 AND 10

(n5-cyclopendadienyl)iron(1+) hezafluorophosphate or polywhe is we repeated using poly(nd-styrene)-Sphate. Exposure time were 120 seconds and 45 seconds 🖷 produce a non-tacky coating uaing the 150 coluene) (n5-cyclopentedienyl) iron(1+) watt rungster spotlight and the 275 matt sunlamp place of in hexafluoroph respectively

described in the before-mentioned Ma.U. thesis and the polyhaving a number average molecular weight of 22,000 in place of mesityless or toluene, respectively. The iron complex 3. Clear, Sog. (chem. Come.) 688 (1873) using palyatyrene The polystytene iron complex was prepared as styrene manifinese complex was prepared as described in 2

⁽d) All countersons are hexafluorquipaghate

Cuenylliscon(1+) hexafluccophosphete (propered in Example 8) using 4-methylbenzaldenyde, 4-methosybenzaldenyde, 2,4-dimethosybenzal-Denyde, 3,4-dimechanydanzaldenyde, cimamaldenyde, and 4-8,N-di-Prepared by first condensing the corresponding aldehyda (i.e., a catalytic amount of potassium hydroxide in aquadus ethenol mechylaminobensaldehyda) vith $(n^6\text{-fluorene})(n^5\text{-cyclopenta-}$ reder nitragen. •

(1+) unit per eight atyrene units and the manganese complex obtained had approximately one (n2-cyclopentadienyl)ironobtained had approximately one tricarbonylmanganese(1+) unit per throe styrene unite.

EXAMPLES 19-51

required to obtain a tack-free coating for each is given in to polymerizing conditions as shown in Table IV. The time and the coating dried as previously described, and exposed compositions and the organometallic salts listed in Table IV. Each solution was coated onto primed polyester film described in previous examples using the polymerizable Polymerizable solutions were prepared as Table IV.

9

<u>ė</u>	-	Lonic organization complex selt (f) sentemp(g) Oven st 75 c	2(0) Own at
3	5.6.7.8.8a.5a)£lucrane]pte(n5-	e) (n ^{t.} nej tale(n ^{2.}	
	cyclopentedieny))dilron(3+)	(A) (34)	
R	(1) Dia(n		8
	head luceuptragheta	greater than 30 min	
ส	(1)bis(nf-meitylens)irm(2+)	Scon(2+) greater then	3
	hexaf luornamenate		S.
a	() bis(n6-mesitylone) iron(2+)	(scin(2+)	
	heraf luorgant japonata	988 S	•c 10 min
R	(K.) Dis(no-heramethy) beneated action (2.)	Management (10)	

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· .	õ	Ionid oromometallic complex asta(f)	
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~	٠	hexafluoritaintinonete 20 mm	
	'n	(m) (g-ally1) (n5-methycyclopentedieny)-	• • • • • • • • • • • • • • • • • • • •
	· ·	m(1+) heraflugeo	
<i>:</i>	: :	er seepato 15 miles	
	2	(n) (m-allyl) (n-methylcyclopentationyl-	
2		dioapponylmengenees(1+) hexaflucto-	
		prospete 30 min	
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	ĸ	(n) (decyclobasedie-22) tricestressiirre(1+)	
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	1	4 ,(0)	
:	8	(-cyclonopeatriany))trionchonyl-	
ST .	•	Christian(1+) hexaClassrephosphate 15 min	
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	2	(0) (F-cyclohepteteleny)) trioacteny)-	
		chreaten(1+) heusthercoursethes 30 mec	
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	R	(o) (P-cycloheptetrieny)) triomatony)-	
٠.		chreatus(1+) hexaflarycoantisposets 15 sec	
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2	#	(O) (D'-cyclicheptetrieny)) trionepuny!-	
		molyddenue(1+) hemefluor.erumane 30 mec	
	:		
:	×	(o) (1 -cycloheptetrieny))tricestonyl-	
		tungten(1+) hexafluornarienese 15 min	٠
	;		
;	3	(P/ pr-toluene) trioartony lagrange (1+)	,
Ç	•	hexaelluorqphagae	

3	tripherylatibinal.com(1) tetrafluccompresser than borate 60 min 61 (0)hemacartorylthenium(10) hema- fluctomatimonata/hydronypastaflucro- antimonata	10 65 (*)(n ² -cyclegentadiaryl)tribartonyl- iron(1+) hemafluoronni jenembe 10 sec 30 mia 66 (t) (n ² -methylopologentadiaryl)dicar- bonylni trosylamogeniase(1+) hemafluoro-	promptate 15 47 (t) (n ² -methyloye)openeadlamyl) dicar- borylaitromylmangeness(1+) hemaflucer- artimonate (u) (n ² -million) (n ² -cyclomylouser) 11 mc (1+) hexaflusonemess 13 mc 15 mc 16 mt (1-) hexaflusonemess (1-) hexaflusonemess	*-yclopatkadionyl)isos- enuts n ³ -cyclopenkadionyliisos spiets	91 (V) [gris("A-bensencotals) dicartoxy]}- 25 (1+) heartluoroset incesse 130 sec
5.1					
Ex. Emic Organization (Complex sale(f) sanismy(g) oven at 75°C and substance (left contraction of the contra	15 (@) (n6-meitylene) tricattory lithenium(1+) theneflucroarrenate 15 (n5-cyclopentationy 1) dicartory 1- triphery lattory than ghina from (1+)	210 mcc (F) 012-cyclopeneadlory1) dicartory1- Efficiely1phosphine iron(1+) Manafluoricaeneae	15 tripmer/phosphineiron(1+) ***********************************	20 (C)(q^-cyclopestadiany))dicarbony)- triphenylet.bluesisma(1+) beatfluorient.immate 41 (C)(q^-cyclopestadiany))dicarbony)- triphenylet.bluesism(1+)	25 temperatures and (1) temperatures (2) temperatures (3) temperatures (3) temperatures (3) temperatures (4)

ies 22 and 51 in which 2 parts of nitromethans composition, and I part of acetonitrile with and dioxido, 5 parts of 3,4-spospeyelohenylastbylples 19-21 is which 2 parts of scetoniurile art of the sonic complex in a mixture of 5 parts of Contings were safe as described in previous emplos using by AL P.

the sedag a 275 wett G. E. Sanlamp at a distance of 10 on from the conting.

nos with the procedure outling

ENLIS OF 186, 36 (1980).

2. Orn. Ste. (Chen. Com.) 500 (1971).

1 307 (1944)

4c Brath, 6, 112 (1960).

3. Summerille Com, 13, 10 (1960). Ė

1. One. For. (One. One.) 311 (1941).

F. Crarle 72, 529 (1983).

Br. Cree. 5, 1037 (1964).

Ber. (Om. Om.) 648 (1975).

Om L 83 (1962).

2. morn. mel. Com. J. 165 (1955) and laptin. Chm. S. 1177 (1966). 3. 48. Chim. Sec. 29, 478 (1977).

mentile destanting A. R. D. King, Academic Press, N.Y. 1965. mirichada, M.A. thesis, U. of Florids (1978). 2. Och. fest. 69, 1170 (1950).

EXAMPLES 52-63

catalysing the polymorization of cationically polymerizable of sonic selt as shown is Table V. Lach misture was coated percent by weight, based on total weight of stock solution, compounds, solutions were propered as described previously unto polytvanyladene chloride primed polyeeter sheeting, dried, and exposed to the radiation of a 275 watt G. E. consisting of secot neletion, solvest, and 10.0 to 0.01 toute sales of organostallic completes effective for To illustrate the reage of concentrations of 30

non-tacky to the touch. The results are given is Table V. sunlamp at a distance of lo ca until the costing was

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	nic ocom	altyle.	3		sityle	3	altyle.	3	· -		Meln mestylene) iron(2") In	2		•		3	Continu	•		Н	•	2		(n2-cycloxentellow))dicarbon)-	telphenylet (himmirracija)				(n'-cyclopentableny);dicarbonyl-	tright Wastiblestronii+) heastlore	6
		AF)	and lateral			ant imprate		and largers				Section.		54	A CACTODEN	to Section	beneft tuproment		(M. exclosere	er labora las ibi				(a Cycle	telpheny)	1			(ne)c lo	7 A. W. 17.23	ent increte
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medes will become appearant to those atilies in the art ties, and it about to enderstood that this invention Unclose and fications and alterations of this differed departing from the scope and spirit of this 2

is not to be ambig limited to the illustrative ambediment

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Palazzotto, et al 0109851 443,660 EPO/LRS

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mediate atrength mucleophile or upon photolysis capable of organometallic complex cation capable of adding an interelements of Periodic Groups IVB, VB, VIB, VIIB, and VIIIB. liberating at least one coordination site, said metal in said organometallic comp) ex cation being selected from catalytically affective amount of an ionic salt of an An energy polymerisable composition com priming a cationically polymerizable material and a

said ionic salt has a formula selected from Pormulas I, II, The compasition according to Claim 1 wherein **.** and III.

FR

[(T]e)(T3e)(T3e)Wej@[(T]p)(T3p)WpjP-[[L10](L20)(B30)molj[(L10](L20)(L30)md]k-1x01(12)(10100xe wherein Me, Mb, MC, and Md each represents a metal selected from the elements of Periodic Groups IVB, VB, VIB, VIIB, and VIIIB,

each capable of centributing two to twelve W-electrons unsubstituted ecylaic and cyclic unsaturated compounds ligands contributing s-electrons that can be the same eyelle arematic and heterosyclic arematic compounds. and groups and admittuted and unsubstituted carbo-Lla, Llb, Llc; and Lldfeach represents none, 1, 2, or 3 or different ligades selected from substituted and buclear, or tetranuclear complex with the proviso that persula I can represent a mono-MAND, MANDEC, or MANDED to the valence shall of Me, Mb, Mc, and Md respectively with theif attendent ligands, Ly perpound comprising ma Auclear, biamelear, tri respectively

ligande contributing an even number of d-electrons Lis, Lib, List and List mach represents none or 1 to 6

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41-. and tel-dentate ligand., each contributing 2, 4, that can be the same or different selected from sono-ME 6 -- alsoctrons to the valence shall of Me, Mb, Mc, and ord managed toply,

LPb, LPE, and LM each represents move, 1 or 2 ligands sentributing one e-electron each to the valence shell of are, ire, att, and ard respectively,

-electrons to the valence shells of two or more metal s-elections that can be the same or different ligand resents acre or 1 to 6 bridging ligands containing selected from embatituted and unsubstituted acyclic scheengelic enometic compounds, each capable of ed cyclic enseturated compounds and groups and oring as a bridging ligand contributing 2 to 24

as seen seeming of d-slacerons that can be the same or Migrada, each deserted 2, 4, or 6 and leathons to the malesco aballa of two or more metal atoms Nº, Nº, Nº, different enlacted from mone, di, and tri-dentate or of stantementy;

with the provide that the total electronic charge contributed sents sees or 1 to 12 bridging ligands contributing 1. 2. Je or d - alectrons to the valence challe of two cas, the, the, the, the, the, the the the said to plus or mare matel atoms me, mb, mc, or me elemitaneously; the man of londe charge on me, mb, me, and me results in a meddant are practeins charge of a to the complex;

o do es integra baying a value of 1, 2, or 3, the residua electrical charge of the complex cations

K is a helogan containing complex anion of a metal or

f is an integer of 3 to 3, the number of complex anions requires to apetralise the charge e on the complex Cation, and

n.), and k independently are 0 or 1, with at least one

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3x0+ (44(01)(21))

Were in

contributing two to twelve s-electrons to the velence eslected from substituted and unsubstituted acyclic and alloyollo unsaturated compounds and groups and L' represents none, one, or two relectron contributing ligands that can be the same or different ligand heterocyclic aromatic compounds, each capable of We represents a metal selected from elements of the Periodic Groups IVB, VB, VIB, VIIB, and VIIIB, substituted and unsubstituted carbocyclic and shall of MP,

provise that the total electronic charge contri-Le represents none or 1 to 6 Mands that one be the age or filtferent ligand selected from mono-, di-, and dentate liganda, each contributing 2, 4, or 6 A residual net positive charge of a to the buted tel mm by L7 and L0 plus the lonic charge on me Octrone to the valence shell of MP; recults

es E and f are as defined above; and

((L9)(L10),P) *9r,

ents a matel selected from Cr. Mo. W. Mn. Ba. Po. 18 Per de Traped where in

that can be the same or different ligand selected from supptituted ne-bensene compounds and compounds having B 4 fused rings each capable of contributing 1 to L9 reprepents one oritio --electron contributing ligands **-aromatic compounds selected from 16-bensene and 45-mydlopentadiemyl, and a7-cyclohaptatrienyl and substituted and unsubstituted allays,

"electrons to the valence shell of MP;

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come and, and, and, or and administrationally;

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of them being equal to 1,

0109861 Lie represents none, 1 to 1 . wands contributing two

with the provide that the total electronic charge O-clectrons to the valence shell of MP;

We on all smealts is a residual not positive charge of q contributed to up by ligands L' and L'lo, plus the lonic a the employe

E is an integer baying a value of 1 or 2, the residue!

T is a bologen containing complex anion selected from cleaterical charge of the complex actions

a is an integer of 1 or 2, the number of complex anions re-AMOUT. BIFGT. and Birgon., and

guires to sectralise the charge q on the couples cation,

3. The amposition according to claim 2 wherein is December 1, the ligands Lie, Lib, Lie, and Lid of the -

each emetains less than 100 carbon atoms and up to 10 betach atime melected from mitrogen, swifur, ourgen, phospherus, ermeals, beleatum, antimony, tellurium, sillion. Commanden, tin, and borons

the Mannes Lib, Lib, and Lid of the lonic salt sech

ittenic, selenius, antique, tellurius, and adydentate ligands expuble of forming with mandemetate ligands having up to 10 carbon in attropia, miller, caypen, phosphorus, Penesie, moleniem, antimosy, tellurium, in Amendaling up to 10 hotory atoms solveted fine attention, millur, anyon, phesphorus, otems and up to 18 hotero atoms selected President acturated or uncaturated file meat #4, 40, 40, or 14 a t., 5., or littles to the metal stony

the ligands (No. 178, 126, and 124 of the ionic salt sach has up to 10 certain stems and up to 10 hotors stems

0109851 selected from nitrogen, sulfur, oxygen, phosphorus, ersenic, selenium, antimony, tellurium, silicon, Vermentum, tin, and borons

The Parketon

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the bridging ligand L4 of the ionic salt contains less than 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen and nitrogen, sulfur, oxygen, phosphorus, ersenic, selenium, entimony, tellurium, silicon, germanium, tin, and boron;

the bridging ligand L⁵ of the ionic salt contains up to 30 Carbon atoms and up to 10 betero atoms selected from nitrogen, sulfur, oxygen, phosphorus, ermentc, selenium, antimony, tellurium, and botton; and

carbon atoms and up to 10 hetero atoms melected from selegium, antimomy, tellurium, ellicom, germanium, bridging radical L⁶ of the ionic salt has up to 10 nitrogen, sulfur, oxygen, phosphorus, armenic, tin, and boron; 3

wherein, in formula II

20

Carbon atome and up to 10 betero atoms selected from nitrogen, sulfur, oxygen, mitrogen, selfer, oxygen, phosphorus, areasic, selenium, antimose, tellurium, ligand L7 of the lonic salt contains less than 100 siliann, germanium, tin, and boron;

ligand L⁸ of the lonic salt is selected from:

amtimosy, tellurium, ellicun. germanium, tin, and monodentate ligands having up to 38 carbon atoms and up to 2 betero atoms selected from nitrogen, selfur, ouygen, phospharus, araunto, selenius, Moron, and

unsaturated ging containing up to 10 hetero atons polydentate ligands capable of forming with metal Me de, Se, or 6-membered saturated or

tallurium, ailicon, germanium, tin, and borom in photophorus, armenic, selenium, antimony, selected from nitrogen, sulfur, oxygen, addition to the metal atom; and

III dimine in Permits III

ligand L¹⁰ of the ionic sait is selected from carbon ligand L⁹ of the ionic salt contains up to 24 carbon and up to two heterostoms selected form nitrogen, months and the attrosomium ion, and and milfur.

Mydrocarty learbony 1, Mydrocarty learbonaaido, phany 1, aso, The composition according to claims 2 and atoms and up to 10 betero atoms selected from nitrogen, auliur, orygen, phohphorus, ersenic, eclenius, astimony dimeth_lamino, diphenylphosphino, trimethylsilony, and condensed rings, said group containing up to 30 carbon independently unsubstituted or substituted by a group wherein the ligands Lle, Llb, Llc, and Lld each is tellurium, ellicon, germenium, tin, and boron, and boryl, halo, hydrony, cyano, nitro, nitroso, oso, Mydrocarbylmarcapto, hydrocarbylosycarbonyl, melected from bydrocarbyl, bydrocarbyloxy, 2

hydrocarbylcarbomyl, bydrocarbylcarbonamido, phenyl, aso, sultur, oxygen, phosphorus, arsenic, selenius, antisony, atoms and up to 10 metero atoms selected from mitrogen, diserbylasino, diphonylphosphino, trimethylsilony, and condensed rings, said group containing up to 30 carbon wherein the ligand L7 or L9 is substituted by a group boryl, halo, bydrowy, cyano, nitro, nitroso, ouc, selected from hydrocarbyl, bydrocarbylomy, tellurium, milicon, germantum, tin, and boron, hydrocarbylmercapto, bydrocarbyloxycarbonyl,

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othylenically-unceturated hydrocarbons, eyelic fermals, and merein seid polymerismis - eterial is melected from The composition according to any proceeding lic others (also designated as 1,2-, 1,3-, and group sentaining meterial, 1,3- 1,3-, and 1,0-offices), viryl others, k-vinyl ompound syclie organosilomenes.

The composition according to any preseding claim wherein said sait is present in an amount in the range int 0.01 to 26 weight percent of seld entimideally Polymerisable meterial. .

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claim further comprising in the range of 0.01 to 10 parts 7. The composition according to any presenting by weight of a spectral sensitizer per part of etallic salt.

8. The composition according to claims 2 to 7 LMb, LMc, LMd, L4, L5, and L4 Migands independently are Stoupejon a polymeric chain.

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to any proceeding claim, sold process samprialing schiulng said entionisally polymericable material with a catalyticably affective mount of eals lonic salt of an organs A process for polymeriaing the conmetallic complex, and

cuelds the resulting admixture with a the or estinic residetion source, 10. A compound according to Claims 2 to 7 having the formula:

[(L9)(L10)NP) +qx

wherein

MP represents a metal selected from Cr. No. W. Mn. No. Po.

La represents 1 or 3 ligands contributing s-electrons that can be the same or different ligand selected from submittuted and unsubmittuted al-allyl, as-cyclopents dianyl, and q7-cyclohaptatrianyl and submittuted af-aromatic compounds selected from af-bensene and electrons to selected from af-bensene and aubmittuted q6-bensene compounds and compounds having 2 to 4 fused rings each capable of contributing 3 to 12 electrons to the valence shall of MP;

Lio represents none or 1 to 3 ligands contributing an eventuaber of e-electrons that can be the same or different ligand selected from carbon monoxide or nitrosonius;

with the proviso that the total electronic charge contributed to MP by L⁹ and L¹⁰ plue the lonic charge on metal MP Feaults in a net residual positive charge of q to the complan, and

@ is an integer having a value of 1 or 2, the residual electrical charge of the complex cation;

25 T is a halogen-containing complex anion selected from Aefe . 806 and 80f50M 1 and

A is an integer having a value of 1 or 2, the number of complex enions required to neutralize the charge q on the complex cation.